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DYEING OF WOOLLEN FABRIC PRE-TREATED WITH TIN CHLORIDE USING YELLOW BLOSSOMS

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ABSTRACT

Woollen fabrics pre-treated with tin chloride were dyed using yellow blossoms from various plants in order to compare their colour and fastness. The influence of tin chloride on wool was studied and its concentration was optimized for the wool mordanting. Woollen fabrics dyed with yellow blossoms of broom, forsythia, rapeseed and dandelions had the highest saturation of yellow colour with an exceptionally brilliant shade and outstanding fastness properties. Given the size of the blossoms, their wide availability, long flowering period and complete harmlessness, we recommend the dandelion as the most appropriate source of the yellow dye for the natural dyeing of woollen fabrics.

KEYWORDS: natural dyes, dandelion, forsythia, tin chloride, fastness, wool.

Introduction

Fabrics dyed with natural dyes represent an attractive alternative to synthetic dyes for some consumers, even though natural dyes have many disadvantages in comparison with synthetic dyes [1]. The low content of dyes in plants makes it necessary to process large volumes of natural material. The low percentage of dye attached to the fibre is associated with low affinity to the fibre. When binding the dye to the fibre rather weak interaction forces, such as hydrogen bonds or Van der Waals forces are asserted; this results in a lower wash fastness. The hues of natural dyes extracted from plants are often cloudy and not brilliant due to the admixtures of other plant substances (chlorophyll, tannins). Also different cultivations and changes of natural conditions during their growth (sunshine, rain, soil type and nutrition) may affect the chemical structure and concentration of the dye in flowers.

Seven kinds of plants with yellow blossoms from the Central European spring countryside were randomly selected for the dyeing of woollen fabrics pre-treated with tin chloride. Following herbs and shrubs were selected: forsythia (*Forsythia intermedia*), broom (*Cytisus scoparius*), yellow azalea (*Rhododendron luteum*), kerria (*Kerria japonica ´Pleniflora´*), rapeseed (*Brassica napus*), dandelion (*Taraxacum officinale)* and leopard's-bane (*Doronicum orientale*). Their overview is given in **Table 1**.

As we have shown previously, most of the yellow flowers in combination with tin chloride dye the woollen fabric to a bright hue of yellow with an excellent ability to protect against UV radiation [2].

The presence of flavonoids and carotenoids usually evokes the yellow colour of the flowers. Both of these groups have a high ability to absorb UV radiation and eliminate free radicals. Various substituents of flavone (2-phenyl-1,4-benzopyrone), e.g. flavones acids and glycosides are present in all of these flowers, as we proved by the reaction with the Folin reagent [2]. However, flavonoids are present in high amounts in blossoms of forsythia [3], broom [4], leopard's-bane [5] and yellow azalea [6]. Other flowers of tested plants (kerria [7], rapeseed [8] and dandelion [9]) contain a larger proportion of carotenoids and xanthophylls (carotene, lutein), which are derivatives of tetraterpene.

Table 1: Overview of the plants whose yellow blossoms were tested for dyeing of woollen fabrics

Plant	Family	Description	Flowe-ring period	Weight of blossoms
Forsythia	*Oleaceae*	shrub, cultivated	IV - V	0.04
Broom	*Fabaceae*	shrub, wild	V - VI	0.1
Kerria	*Rosaceae*	shrub, cultivated	IV - V	0.6
Rapeseed	*Brassica-ceae*	herb, cultivated and wild	IV - V	0.03
Yellow azalea	*Ericaceae*	shrub, cultivated	V - VII	0.3
Dandelion	*Astera-ceae*	herb, wild	IV - X	0.8
Leopard's-bane	*Astera-ceae*	herb, cultivated and wild	IV - V	0.7

The fastness, brilliance and depth of the hue of natural dyes can be increased by using a suitable mordant with which the subsequent dye creates a complex. The result is a hyper- and bathochromic colour shift [10]. One of the mordants is tin chloride, a water-soluble inorganic substance with reducing properties. Tin chloride is harmful to the health (acute toxicity is expressed by a lethal dose LD50 administered orally in amounts 700 $mg \cdot kg^{-1}$ for rats, 250 $mg \cdot kg^{-1}$ for mice and 10 000 $mg \cdot kg^{-1}$ for rabbits [11]). It caused changes in blood count, bone demineralisation, inflammation and organ damage in test animals.

Nevertheless, in the Czech Republic and some EU countries the use of tin chloride is allowed for food purposes (designation E 512) [12]. Tin is utilized e.g. as an antioxidant in beverages with carbon dioxide or in the preservation of canned asparagus. However, since it is a harmful substance, it is desirable to minimize its use as a mordant, even though it is only a small amount of tin that comes into contact with the skin.

Materials:

Fresh blossoms of these shrubs and herbs: forsythia (*Forsythia intermedia*), broom (*Cytisus scoparius*), kerria (*Kerria japonica* "Pleniflora"), rapeseed (*Brassica napus*), yellow azalea (*Rhododendron luteum),* dandelion (*Taraxacum officinale*), leopard's-bane (*Doronicum orientale*), woollen fabric (surface weight 156 $g \cdot m^{-2}$), tin (II) chloride ($SnCl_2$).

Methods:

Pre-treating and dyeing of woollen fabrics

Fabrics were pre-treated with a solution of tin chloride at concentrations of 0.5, 1, 2, 3, and 6 $g \cdot L^{-1}$. Mordanting was performed at a ratio of 1:50 (1 g of fabric: 50 ml of water). The bath with fabrics was brought to the boil and then allowed to cool for 12 hours.

Wrung pre-treated fabrics were transferred into the dyeing bath composed of distilled water and fresh blossoms. Dyeing was performed at a ratio of 1:100:20 (1 g of fabric: 100 ml of water: 20 g of fresh blossoms). The dyeing bath was brought to the boil and left boiling for 15 minutes. Fabrics were removed from the bath after 24 hours. The dyed fabrics were thoroughly washed using detergent without enzymes, optical brighteners and phosphates without alkalization and dried at 50°C.

SEM and EDS analysis

Morphological changes in woollen fibres that occurred during the mordanting of fabrics were studied with the morphological aid of SEM. Also the content of tin and of other elements was determined by the EDS analysis, which is a part of SEM (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy). EDS provides a qualitative and quantitative elemental analysis of the sample to a depth of 1-2 microns. The analysis was performed on the SEM electron microscope UHR Ultra Plus (Carl Zeiss).

UV/VIS spectra of extracts from blossoms

Absorption spectra of seven blossoms extracts were measured with an absorption spectrophotometer UV-1600 PC (Mapada, China), in the region of visible light and light of near UV region.

Remission and K/S function

Dyed fabrics were measured on the remission spectrophotometer Datacolor to

obtain CIE L*a*b* colour values and remission (reflectance), from which were calculated the K/S curves (Kubelka-Munk function). Positive values of a* indicate a shift to the red on the green-red axis, positive values of b* indicate a shift to the yellow on the blue-yellow axis.

Two phenomena occur when light falls on the fabric: a part of the light is scattered and absorbed, and a part is reflected. This can be described using the Kubelka-Munk equation **(1)** defined for coloured paper [13]. It can be applied to materials in which more than 50% of falling light is reflected and less than 20% of falling light passes through the material, therefore also for textiles (if a part of the light that passes through the thin fabric must be eliminated as a result of having several layers). The ratio of coefficients K and S is linearly dependent on the dye concentration in fibre and hence is actually a parallel to the Beer-Lambert law which applies to solutions. The calculation is also burdened with a structure and an inherent original colour of the dyed substrate and it is necessary to subtract the K/S value of the undyed fabric from the K/S values of the dyed fabric. In the equation **(1)** K is the absorption coefficient, S is the scattering coefficient, R is the remission in % (100 = total reflection, 0 = absolute absorption of light at a certain wavelength), while the reflectance spectrophotometer records the reflection of individual wavelengths of the entire VIS spectra, i.e. from 380 to 760 nm.

$$K/S = \frac{(100 - R)^2}{2R} \quad (1)$$

Fastness of dyed woollen fabrics
The wash fastness was accomplished by modified procedure based on the standard EN ISO 105 - A01: 2010 - Tests for colour fastness - General principles of testing. The sample was tested with two accompanying undyed fabrics in rotary cartridges of the dyeing apparatus Ahiba Nuance Eco in a water bath of 40 °C for 60 minutes with the addition of a liquid detergent without optical brighteners, enzymes, without pH modification (alkalinisation), and with stainless steel balls. After the separate drying, the colour changes of the dyed fabrics were subjectively evaluated in the grey box under standardised illumination (D45) and expressed in degrees on the grey scale. Degree 5 on the grey scale represents the maximum stability without colour changes; degree 1 represents considerable big change in the hue and the worst degree of fastness.

The light fastness was tested by high pressure discharge lamps Ultramed 400 (Osram) with an output of 8.18 $W \cdot m^{-2}$ in the UVA and 1.71 $W \cdot m^{-2}$ in the UVB radiation using the blue scale of woollen fabrics for the light fastness (EN ISO 105 - B02: 2014 - Colour fastness to artificial light: Xenon arc fading lamp test). Degree 1 on the blue scale means the worst light fastness; degrees 6-7 represent excellent levels of light fastness.

Results:
Mordanting of woollen fabrics
Woollen fabric was pre-treated with different concentrations of tin chloride (from 0.5 g to 6 g per litre). It was demonstrated that higher concentrations of tin salts have a very destructive effect on woollen fibres. Woollen fabric mordanted with tin chloride at the concentration of 3 $g \cdot L^{-1}$ in comparison with fabric pre-treated with the concentration 0.5 $g \cdot L^{-1}$ shrunk in each direction by about 13 %. Higher concentrations of stannous salt (6 $g \cdot L^{-1}$) also caused significant changes in feel (roughness) and a drastic strength reduction of the fabric, in addition to wool shrinkage. **Figures 1 and 2** show SEM images of the untreated woollen fabric and woollen fabrics pre-treated with $SnCl_2$ at concentrations 6 $g \cdot L^{-1}$ for 12 hours.

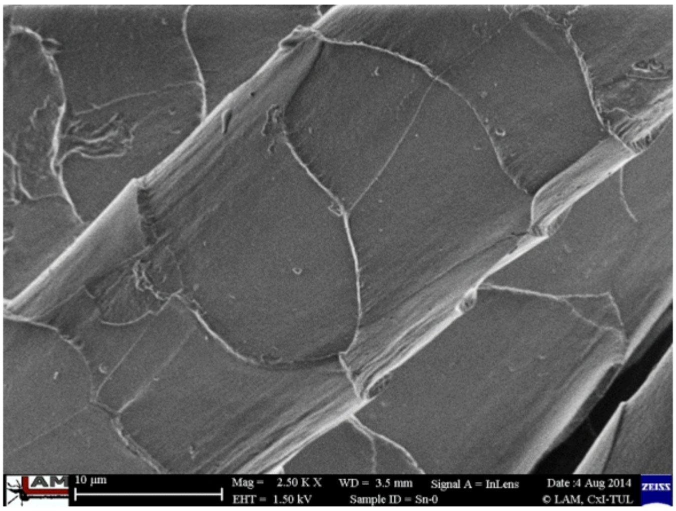

Figure 1: Untreated wool (SEM, 2500x)

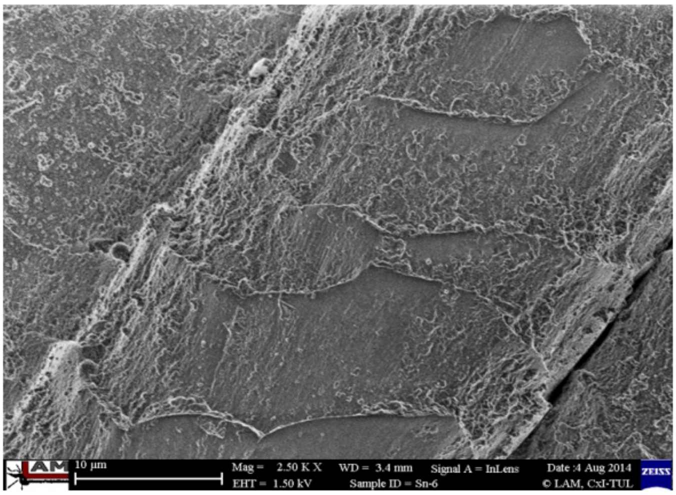

Figure 2: Wool pre-treated with tin chloride at a concentration of 6 $g \cdot L^{-1}$ (SEM, 2 500x)

The EDS elemental analysis of the fibre surface was performed on woollen fabrics pre-treated with tin chloride at concentrations of 0, 0.5, 2, 3, and 6 $g \cdot L^{-1}$ and subsequently dyed with the extract from forsythia blossoms, and on an undyed sample pre-treated only with the highest concentration of tin chloride (**Table 2**). It is evident that the subsequent dyeing process reduced the initial tin content of the most pre-treated fabric (from the original 10.71 to 8.24 atomic %), and also that residue of chlorine on the fibres after dyeing is practically zero in comparison with fabrics only pre-treated without dyeing. This excludes damage of wool caused by the chloramines.

Smaller differences in the content of tin on the fibre surface (from 6 to 24.8 atomic %), which was pre-treated before dyeing with $SnCl_2$ at concentrations from 0.5 to 6 $g \cdot L^{-1}$, confirm that an excessive increase of tin concentration is not effective on undyed fibres after mordanting. This may be related to the damage of wool fibre or the loss of epicuticle due to stannous salt, through which the fibre becomes more hydrophilic (**Figure 2** shows that the treated fibre is swollen, it is thicker than the untreated fibre in Figure 1 at the same magnification). Thus a higher atomic percentage of oxygen is connected with a higher water content bound in the fibre.

Table 2: The EDS analysis of woollen fabrics pre-treated with different concentrations of $SnCl_2$ with and without dyeing

Concentr. of $SnCl_2$ [$g \cdot L^{-1}$]	C	N	O	S	Cl	Sn	Total
	[atomic %]						
blank wool	50.73	21.68	24.76	2.63	0.00	0.00	100.00
0.5 dyed	48.15	15.33	28.41	2.12	0.00	6.00	100.00
2.0 dyed	48.39	13.93	28.19	2.14	0.00	7.34	100.00
3.0 dyed	49.09	12.30	28.95	1.93	0.04	7.69	100.00
6.0 dyed	48.13	12.40	29.34	1.85	0.03	8.24	100.00
6.0 undyed	44.32	16.08	25.15	2.11	1.64	10.71	100.00

Tin chloride is a strong reducing agent that can attack, among others, disulfide bonds in woollen fibres - this can be one of the causes of strength loss. The reduction of disulfide bridges, amine groups and perhaps imines in the peptide bonds of keratin fibres in an acidic environment may also create ammonia gas (NH_3) and hydrogen sulphide (H_2S) which escape during cooking. This may explain why the content of nitrogen and sulphur decreased in the pre-treated and dyed wool (**Table 2**).

Table 3 provides an overview of the L*a*b* values of woollen fabrics dyed with forsythia blossoms extracted at different concentrations of used mordant. The fabric had a nice bright yellow colour after mordanting with a minimum concentration of $SnCl_2$ 0.5 $g \cdot L^{-1}$. The concentration of 2 $g \cdot L^{-1}$ deepened the shade, but with the further increase of $SnCl_2$ concentration in addition to the above changes, the colour shade of the woollen fabric clouded up and acquired a "dirty" tinge. The optimal concentration of tin chloride solution for the mordanting of woollen fabrics is therefore 0.5 - 2 $g \cdot L^{-1}$ at a bath ratio 1:50.

Table 3: L*a*b* values of woollen fabrics dyed with blossoms of forsythia and using different concentrations of tin chloride

Concentration of $SnCl_2$ [$g \cdot L^{-1}$]	L*	a*	b*
0.5	74.5	0.0	60.0
2.0	76.9	-0.5	58.1
3.0	69.0	-0.9	56.2
6.0	63.9	-2.4	52.0

Dyeing of woollen fabrics with yellow blossoms

Table 4 contains an overview of the dyeing results (CIE-L*a*b* values of dyed fabrics using tin chloride at a concentration of 2 $g \cdot L^{-1}$). As is evident from the **Table 4**, hues of fabrics dyed with blossoms of forsythia, broom and dandelion differed especially in lower value of brightness L* (hues of these fabrics were darker and deeper) and also in a very slight shift towards red.

Table 4: L*a*b* values of fabrics dyed with different yellow blossoms (2 g of $SnCl_2$ in litre, 200 g of blossoms in litre, bath ratio 1:100)

Plant	L*	a*	b*
Forsythia	76.9	-0.5	58.1
Broom	73.8	6.4	72.1
Kerria	80.2	-1.3	37.1
Rapeseed	80.7	-0.1	63.0
Azalea	79.4	-0.3	39.1
Dandelion	76.4	3.6	69.2
Leopard's-bane	80.4	0.5	52.6
Undyed wool (blank)	85.3	-1.6	18.4

UV/VIS absorption spectra of extracts from blossoms

Absorption spectra of extracts from blossoms were divided into two images (**Figure 3** and **Figure 4**) according to the similar waveform of their absorption curves with a maximum of about 330 nm (forsythia, broom, kerria and rapeseed) or 340 nm (leopard's-bane, azalea and dandelion). As seen from **Figure 5** tin chloride causes significant change in its spectrum in response to the plant extract immediate (a few drops of stannous salts were added directly to the cuvette with forsythia extract). The hyper- and bathochromic shift of the spectral absorption curves of the extract occurred after the addition of $SnCl_2$, which resulted in the darker and deeper hue of yellow to orange.

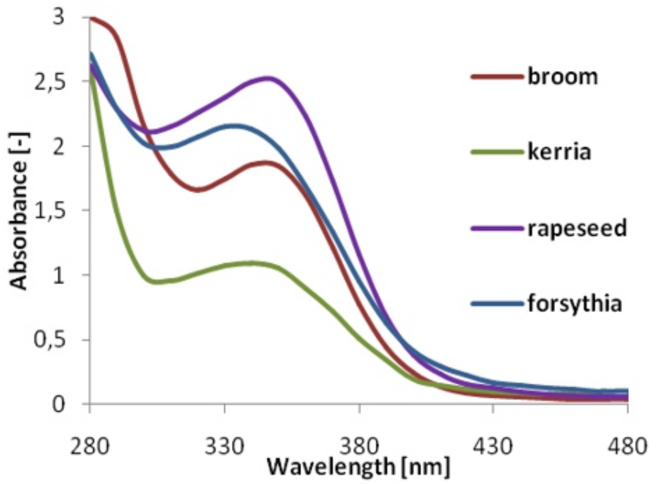

Figure 3: The UV/VIS spectra of rapeseed, forsythia, broom and kerria

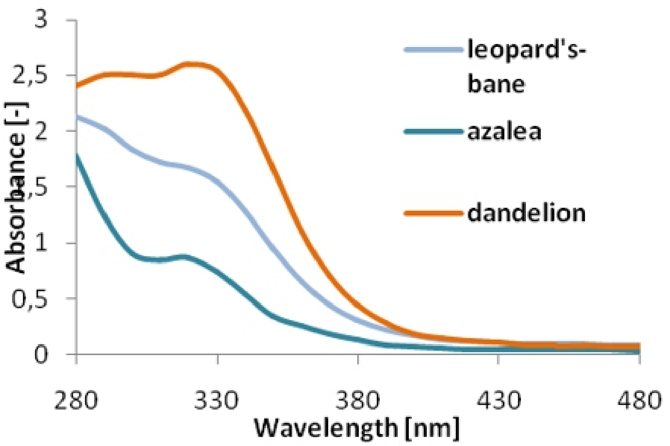

Figure 4: The UV/VIS spectra of yellow azalea, leopard's-bane and dandelion

K/S values of dyed woollen fabrics

The Kubelka-Munk functions (K/S values) in relation to wavelength are plotted in **Figure 6**. It is evident that the maximum K/S functions of all samples were in the area of near UV light and that these values decrease with increasing wavelength. This means that the presence of dyes in the mass of fibres leads to the strong absorption of UV radiation; the light scattering predominates toward longer wavelengths.

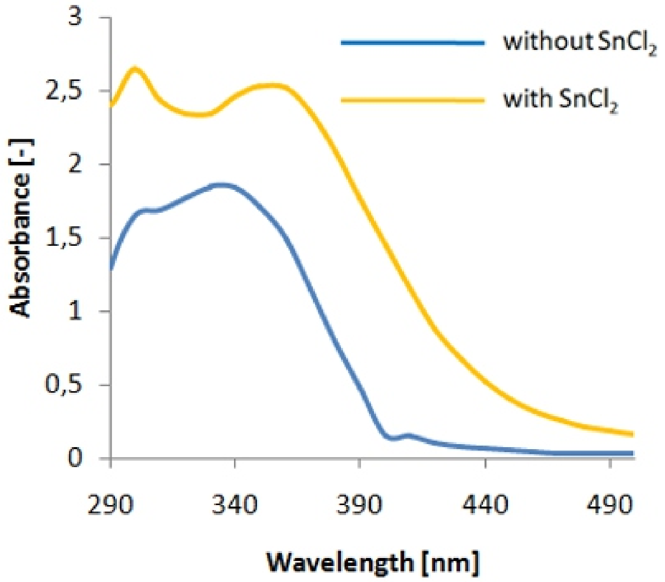

Figure 5: The hyper- a bathochrome shift in UV/VIS spectra of extract of forsythia blossoms after the addition of tin chloride

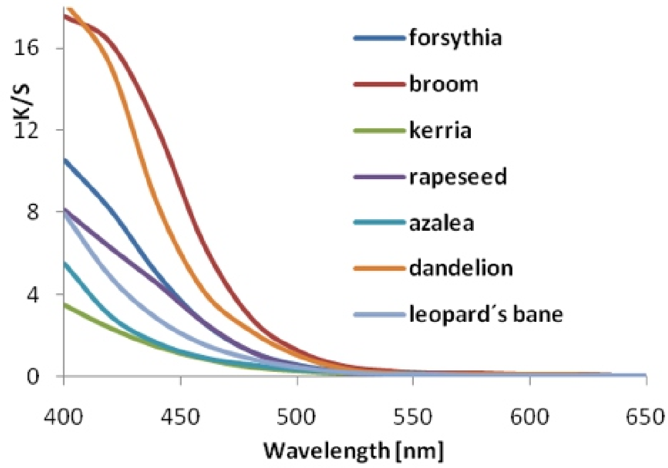

Figure 6: The K/S values of dyed fabrics

Fastnesses of dyed woollen fabrics

The summary of wash and light fastnesses is contained in **Table 5**. All tested samples showed the highest wash fastness (grade 5 of the grey scale) without leaching into accompanying fabrics. Values for the light fastness in fabrics dyed with blossoms of forsythia, rapeseed, dandelion and leopard's-bane where values reached level 5-6 on the blue scale were surprisingly high. This corresponds to several tens of hours of UV radiation and it means an excellent light fastness.

Table 5: Wash fastness and light fastness of dyed fabrics

Plant	Wash fastness[a]	Light fastness[b]
Forsythia	5	5 - 6
Broom	5	5
Kerria	5	4
Rapeseed	5	5 - 6
Yellow azalea	5	4
Dandelion	5	5 - 6
Leopard's-bane	5	5 - 6

Discussion:

Identical weights of fresh blossoms (200 g in 1 litre) were used for dyeing of woollen fabrics pre-treated with tin chloride in a concentration of 2 $g \cdot L^{-1}$. All used blossoms dyed the woollen fabrics to bright yellow colours, of which the strongest colours were obtained with forsythia, broom, rapeseed and dandelion. However, broom is not the ideal plant for dyeing because it is mildly toxic (it contains several cardiotonic glycosides and alkaloids like lupanidine [14]) and its blossom without calyx has a small weight (0.1 g). Thanks to the European

Union and its controversial promotion of alternative energy sources, in recent years rapeseed has been grown on vast areas of European agricultural soil and it also grows wild in many places. It can be considered as widely available, but has a relatively short flowering period and the weight of fresh blossoms without calyx is very small (approximately 0.03 g).

Fabrics dyed with blossoms of dandelion had a bright and deep yellow hue which was very similar to the hue of fabric dyed with broom and forsythia. Moreover, a blossoms of dandelion have the largest mass (about 0.8 g) of all the tested plants; 10 g of fabric in 1 litre of dyeing bath needs about only 250 blossoms in contrast to broom (about 2000 blossoms), forsythia (about 5000 blossoms) or rapeseed (even up to 6 500 blossoms!). Ideally, in order to achieve the purest yellow hues, it is also necessary to eliminate green impurities with chlorophyll like stems, flower beds and chalices.

Dandelion is a widespread weed in the Central European countryside. In addition to the fact that it can thrive in poor soil and occurs from the lowlands to high mountain areas, it is also absolutely safe and nontoxic. Unlike other test plants that bloom only briefly in the spring dandelions blossoms are widely available most of the year because it blooms from spring to autumn (**Table 1**).

Conclusions:

For the dyeing of woollen fabrics with yellow blossoms containing flavonoids and carotenoids suffices the minimum concentration of pre-treating with tin chloride should range from 0.5 $g \cdot L^{-1}$ to a maximum of 2.0 $g \cdot L^{-1}$. Higher concentrations of this mordant adversely affect properties of the woollen fabric and its final hue. We have demonstrated that it is possible to achieve nice yellow shades with high degrees of fastness on woollen fabric using different yellow blossoms containing flavonoids, carotenoids and xanthophylls. Selecting for the seven tested plants (forsythia, broom, kerria, rapeseed, yellow azalea, dandelion and leopard's-bane), the blossom of dandelion is the best candidate for this use. Due to its wide availability, long flowering period, nontoxicity, large blossom, pleasing yellow hue on dyed woollen fabrics and very high degrees of wash and light fastness, dandelion is the ideal material for natural dyeing of wool in Central Europe.

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